TITLE: Structural and Tunnel Characteristics of Langmuir Films Based on Molecular Cluster Nanostructures

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Structural and tunnel characteristics of Langmuir films based on molecular cluster nanostructures

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1 Introducion

In development of nanoscale electronic devices, such as nanoelectronic digital circuits, the single electron tunneling effects and quantum size effects in isolated conducting nanoparticles are of principal importance. Each of these effects can be detected when charging energy and/or electronic level separation exceed the thermal energy k_BT. The manifestation of both effects correlates as a rule with decrease in nanoparticle size. Relevant effects were observed at room temperature in the tunneling current-voltage characteristics in a number of molecular and nanoparticle systems [1]–[8]. The principal point in these studies is the complete characterization of formed structures because random variations of the nanoparticle size and/or shape can lead to unpredictable and nonreproducible changes in the parameters of tunnel system.

Scanning tunneling microscopy (STM) allows to visualize the molecular nanostructures and to study redox processes in single molecules. The molecular structure of samples for investigations of single nanoparticles by this technique has to be monolayer on the conducting substrate.

We have proposed the approach based on the use of mixed monolayer Langmuir–Blodgett (LB) films consisted of inert amphiphyle molecular matrix and guest cluster molecules to create the reproducible stable planar nanostructures with various systems of electron tunnel junctions.

In present work the various supramolecular nanostructures based on the multicomponent LB films of stearic acid (SA) and a number of incorporated clusters have been studied by means of STM technique at room temperature. All clusters were chemically synthesized and hence had atomically equal structure and reproducible properties. Mixed monolayers on the water surface have been studied. The effects related to single electron tunneling and energy quantization of electrons were observed in formed molecular structures.

2 Experimental

The cluster molecules used: carboran ($C_2B_{10}H_{12}$); metallorganic cluster molecules of the close types: $Pt_4(CO)_5[P(C_2H_5)_3]_4$ — cluster I, $Pt_5(CO)_6[P(C_2H_5)_3]_4$ — cluster II, $Pt_5(CO)_7[P(C_6H_5)_3]_4$ — cluster III. Metallorganic clusters have metal nucleus surrounded by organic coating [10]. It provides the stability of cluster structure and tunnel barrier with fixed parameters.

The STM topographic measurements of the monolayer films deposited on a HOPG surface were performed using a Nanoscope-I with homemade control unit scanning tunneling microscope. The cluster molecules were studied spectroscopically by recording

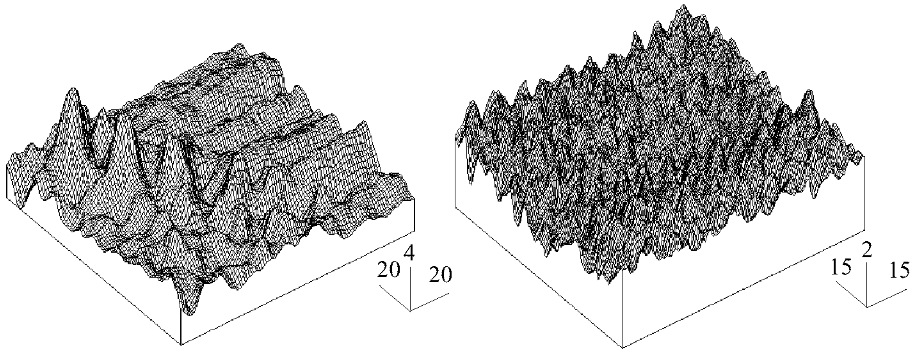

Fig 1. STM topographic images of mixed monolayers of molecular metallorganic clusters (a) $Pt_4(CO)_5[P(C_2H_5)_3]_4$, (b) $Pt_5(CO)_6[P(C_2H_5)_3]_4$) with stearic acid deposited by Shaefers method onto the surface of graphite substrate. $T = 300$ K.

tunneling current-bias voltage (*I–V*) curves in double tunnel junction geometry, where cluster is coupled via two tunnel junctions to two macroscopic electrodes (HOPG substrate and the tip of a STM). The measurement procedure consisted of the obtaining of topographic image and then positioning the tip above an isolated cluster molecule for the tunneling spectroscopy measurements.

3 Results and discussion

Mixed monolayers consisting of SA and clusters I, II and III reveal complex behavior not typical for mixed monolayers with immiscible components, where monolayer properties are weighted mean of the individual values [11, 12, 13].

Fig. 1 shows topographic STM images of different mixed SA/melallorganic cluster monolayers with characteristic observed structures: a chain of cluster I molecules (Fig. 1a), high ordered two-dimensional array of clusters II (Fig. 1b). The single cluster molecule and groups of clusters were also observed. Images of mixed carboran/SA monolayer (molar ratio 1:20) were similar to shown on Fig. 1b. The STM image of cluster molecules corresponded qualitatively to the size of molecule known from the structural data [10].

Spectroscopic results, namely the *I–V* and dI/dV characteristics are shown in Fig. 2. The curves with steps of variable widths and heights (the typical one is shown in Fig. 2 (a, b)) were observed only on the organo-metallic clusters, whereas identical smooth *I–V* curves without noticeable particular features (Fig. 2(c)) were obtained everywhere else except over the cluster molecules. The *I–V* curve shown in Fig. 2(c) is characteristic for single tunnel junction STM tip-substrate and its super linear course is usual for tunnel junctions [14]. All *I–V* curves obtained on different points of carborane/SA monolayer surface (including clusters) were practically identical to one presented in Fig. 2(c), resembled those for single tunnel junction and pointed out the close direct electronic contact of carborane molecules with the graphite substrate. The same effects are known for fullerene molecules deposited onto metallic substrates [8]. The conductivity (dI/dV) curve (corresponding to the *I–V* curve (a) in Fig. 2) is presented in Fig. 2(b), and apparently reveals the complex molecular level structure of ionized cluster states in processes of DTJ tunneling. This *I–V* curve is determined by the tunnel junctions parameters, the energy separation of highest occupied molecular orbital

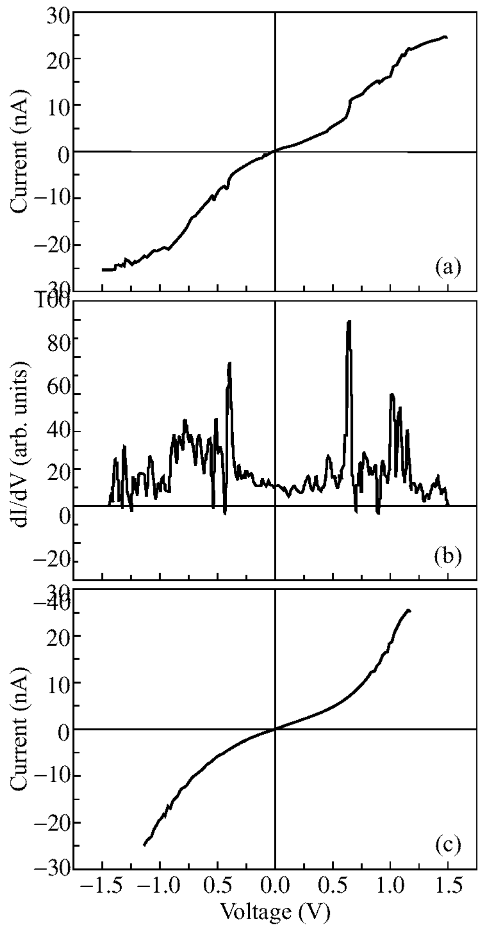

Fig 2. STM tunneling current–voltage $(I-V)$ characteristics of mixed monolayer of cluster molecules $Pt_4(CO)_5[P(C_2H_5)_3]_4$ with stearic acid in ratio 1:80 recorded in double tunnel junction system STM tip-monolayer-graphite substrate at 300 K: (a) characteristic $I-V$ curve recorded on the cluster; (b) tunneling spectroscopic dI/dV curve corresponding to curve (a); (c) typical $I-V$ curve recorded on the monolayer surface without metallorganic clusters.

(HOMO) and the lowest unoccupied molecular orbital (LUMO) and its combination with Coulomb single-electron charging effects during tunneling. The *I–V* picture can be complicated also by molecular orbital anisotropy when tunneling current is correspondingly dependent on the tip position over the molecule and on the molecular space orientation with respect to the substrate surface. To describe quantitatively the course of DTJ *I–V* curve, it is necessary to solve corresponding quantum-mechanical problem taking into account foregoing circumstances.

The curves with steps (the typical one is shown in Fig. 2(a,b)) may be interpreted as a result of single-electron tunneling in DTJ system. The size of the cluster is about 1 nm and the capacitance of the tunnel junctions can be estimated as 0.5 aF $(5 \cdot 10^{-19}$ F) [3]. This value gives the value of Coulomb blockade about 0.5 V which is close to the experimental value (Fig. 2(a)). From the Fig. 2(b) one can see that the steps on the branches of I–V curve are close to periodic with the period of about 350 mV. This value is consistent with the results of the work [14] in which the period of steps on I–V curve of molecular SET transistor on the base of twice larger cluster was approximately twice smaller. These facts give evidence that steps on the I–V curves may be due to the single electron tunneling effects.

4 Conclusions

The approach based on the use of mixed LB films consisted of inert molecular matrix and cluster molecules is effective for formation of reproducible, stable, ordered planar nanostructures with different systems of electron tunnel junctions. The effects of single electron tunneling and/or discrete electronic levels spectrum can be observed and studied in such structures at room temperature.

Acknowledgments

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